

RAW MATERIALS

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BIOCHEMICAL METHOD OF IRON REMOVAL AND ITS EFFECT ON THE COLOR CHARACTERISTICS OF PORCELAIN STONE

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A two-step technological scheme for removing iron from porcelain stone is presented: a combination of biological and chemical reduction of iron in stagnant and washing water regimes. The whiteness of porcelain stone increases after aging as well as after subsequent iron-removal operations with differing contributions: washing with ammonia oxalate > magnetic separation > washing with water.

Key words: porcelain stone, clayey materials, biological reduction, gleification, iron minerals, enrichment.

Large amounts of clayey materials (CM) are used in the ceramic industry. The commercial cost of this raw material largely depends on its whiteness. However, because of the content of mineral coloring impurities, primarily iron minerals, much of the CM is not white and is not used in the production of porcelain articles.

The aim of the present work is to determine the possibility of used and optimizing a technological scheme for biological enrichment of CM and studying their coloristic properties before and after heat-treatment.

The problem of increasing the effectiveness of iron removal from clayey materials involves the solution of a number of problems: the determination of the coloring power of iron compounds differing by state and structural organization in the initial CM before and after their partial removal, including the effect of heat-treatment on the color characteristics of CM before and after enrichment, and the identification of iron compounds in CM, which makes it possible to pick a method for removing them and evaluate its effectiveness.

Coloring of Clayey Materials. The color of CM and the effectiveness of iron removal by one means or another depend not only on the total content, physical-chemical properties and the state and structural organization of the iron compounds but also on the transformation of the iron compounds at different steps of enrichment. The variations of the state of iron in CM are due to valence, coordination, character of the arrangement of the ligands, particle size and so on. The iron

compounds present in CM are usually found at four levels of the structural organization: magnetically dilute (in silicates — ‘silicate’ iron, in organic compounds and paramagnetic minerals), molecular-cluster, superparamagnetic and crystalline magnetically ordered.

The theory of the color of minerals is quite well developed. However, it is not always clear which iron compounds in any particular case determine the color of CM. As total iron in CM increases, it is the iron content mainly in second and third levels of the structural organization that increases. This is completely understandable since clayey minerals have a limited capacity to incorporate chromophoric ions in their structure (for example, kaolinite to 0.5 – 0.6 wt.%). For this reason the color of CM depends mostly on the iron compounds in the second and third levels of the structural organization and less on the coarse-crystalline, magnetically ordered particles (fourth level). But, at the same time, the amorphous and weakly crystallized iron (hydr)oxides are strongly bound with clayey particles and their magnetic susceptibility is low. In this connection the effectiveness of their removal by conventional methods is, as a rule, very low.

Choice of Technological Scheme for Removing Iron from CM. There are three methods for removing iron: physical, chemical and biochemical, the latter being new [1, 2].

The main chemical methods are treatment in gaseous media [3] or in a solution of mineral [4] and organic [5] acids or a two-step treatment with the addition of reducing agents [6].

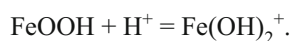
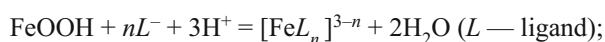
Some components used for treating CM, for example, treatment in a chlorine gas stream [3], have an adverse effect on the environment.

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Chemical dissolution of (hydr)oxide particles depends strongly on the acidity of the media. Under neutral conditions it develops slowly, so that one of the main drawbacks of removing iron by treatment in mineral acids is the need to maintain a low pH for a long time [4]. Under such conditions the clayey minerals become saturated with hydrogen ions, the particles become loosely packed and, in consequence, the technological properties become degraded — the strength of the intermediate product, the plasticity of the clay bodies and the casting properties of the slip based on them all decrease.

It is best to use weak organic acids (oxalic and citric acids) to dissolve iron (hydr)oxides or to preserve the structure of clayey minerals [5–7]. In order to fully use the possibilities of organic compounds it is necessary to pick the ones that fulfill three functions: 1) act as reducing agents, 2) form complexes with iron, and 3) increase acidity, dissolving (hydr)oxides because of the high activity of H^+ . As a result, iron (hydr)oxides are affected by three chemical factors [8]:



Acidic ammonium oxalate possesses such properties. It is a Tamm reagent with $pH = 3.2$, which consists of a mixture of oxalic acid 0.14M $H_2C_2O_4$ and ammonium oxalate 0.20M $(NH_4)_2C_2O_4$ [9].

To study the chemical solubility of goethite these factors were arranged in the following order: reduction > complexation > protonation [8, 9].

When ammonium oxalate is used with a neutral medium protonation has no effect, which better for treatment of CM [1]. The dissolution of iron (hydr)oxide particles is controlled not only by the activity of protons (pH) but also by the activity of electrons (Eh): it is precisely the high activity of electrons that determines the Fe(II) concentration in the dispersion medium during enrichment.

The abiotic (chemical) dissolution by ammonium oxalate with a neutral dispersion medium is very slow, but such a medium does impede the vital activity of microorganisms in the biological reduction of iron (hydr)oxides. In this case a technological scheme with a two-step method of removing iron from CM combining the biological and chemical methods is used [1].

Biological reduction $Fe(III) \rightarrow Fe(II)$ and subsequent dissolution proceed in the course of a complex heterogeneous reaction consisting of several steps: 1) interaction of donor and acceptor of electrons — iron hydr(oxide); 2) transport of electrons; 3) dissolution of hydrated Fe^{2+} ; 4) Fe^{2+} diffusion from hydrated iron. According to [8, 9] the second step determines the rate of total reduction.

Microorganisms effecting the reduction of iron (hydr)oxides. Biological iron reduction has the main effect on the dissolution of Fe (hydr)oxides, which is used in the development of CM enrichment technology [1, 2, 10, 11]. Iron re-

ducers use different physiological and biochemical processes to reduce insoluble Fe(III) (hydr)oxides in neutral media [12].

An large group of microorganisms, including bacteria of the type *Bacillus*, *Desulfovibrio* and others as well as fungi of the type *Actinomucor* and others [13], is capable of effecting fermentation and transferring to Fe(III) part (about 5%) of the reduced products of metabolism.

Dissimilation iron-reducing bacteria (DIRB), which use Fe(III) as an electron acceptor, oxidizing organic compounds as a source of energy and growth in many geochemical media, have been described in recent years [13]. The most studied DIRB are *Geobacter* and *Shewanella*.

The mechanisms of electron transport to the acceptor Fe(III) have been little studied. But, considering the diversity of microorganisms in CM it is very likely that diverse processes occur in the reduction of Fe(III) [12].

On the basis of the mechanism describing iron reduction by microorganisms it has been found that organic compounds participate in this process in two ways.

Participation of organic compounds in the biological reduction of iron (hydr)oxides. According to [14], organic compounds fulfill previously unknown functions in the process of bioreduction of Fe(III) as a source of energy and an electronic shuttle. In addition, investigations performed by microbiologists and soil scientists in the last ten years on the nature of gleification make it possible to understand the particulars of the transformation of iron compounds in water-logged CM.

Gleification and bioreduction of iron minerals. Gleification is a combination of chemical and biological processes occurring in the case of CM in a reduction state in stagnant or stagnant-washing regimes [9, 10]. In [1, 11] it is shown that gleification of CM promotes not only the reduction of iron but it also improves the rheological properties of CM.

EXPERIMENTAL PART

Biochemical method of iron removal from porcelain stone. The direction of biochemical processes during aging accompanied by gleification of PS and bioreduction of Fe(III) is determined by a combination of factors [10]: the moisture content of the suspension, presence and composition of microorganisms, composition and content of the nutrient medium used to develop natural microflora, and the temperature regime.

A variant with a combination of bioactivation of a natural cenosis of the microorganisms present in CM and the use of an inoculum chosen beforehand from Prosyantovskoe kaolin was chosen to analyze the bio-treatment methods [11]. The technological scheme for treatment of PS included two successive water regimes — stagnant and washing.

Two schemes of the chemistry of gleification are distinguished depending on the water regime:

— in a stagnant water regime (aging process) gleification is accompanied by the reduction of Fe(III) as an electron ac-

TABLE 1. Physical-Chemical Characteristics of the Nonmagnetic Fraction of Porcelain Stone Samples at Different Steps of Enrichment

Sample	Fe ₂ O ₃ content, wt. %	RC,** 10 ⁻⁶ cm ³ /g	EPR signal,*** arb. units
1*	0.27	44	1.00
2	0.26	23	0.95
3	0.23	17	1.70
4	0.22	22	1.45
5	0.18	8	0.45
6	0.16	2	0.30

* Control sample.

** Reducing capacity of iron oxides.

*** $g \sim 2.0 - 3.0$.

ceptor; newly formed Fe(II) either precipitates in the form of Fe(II) minerals or it is adsorbed on the surface of clayey materials and iron (hydr)oxides [15]; for example, in the case of the biological reduction of goethite the Fe(II) accumulation limit corresponds to a volume typical for the sorption of a bivalent cation; the inhibiting effect of adsorbed Fe(II) on the surface of (hydr)oxides and the cells of iron-reducing bacteria explains the conservation of crystalline (hydr)oxides under anaerobic conditions of a stagnant water regime of CM;

– in a washing water regime the reduction and dissolution of (hydr)oxides are greatly accelerated owing to organic ligands obtained from different sources (metabolites of microorganisms or a component added into the system), which form complexes with Fe(II) [15] and are removed from the system in a washing water regime [1]; when Fe(II) is removed from the system the equilibrium between the dissolved and sorbed Fe(II) shifts so that the inhibiting effect of Fe(II) sorption decreases.

Materials and methods of investigation. Porcelain stone from the Gusevskoe deposit (Primorskii Krai) with the following composition (wt.%) was chosen as the object: 76.70 SiO₂, 17.08 Al₂O₃, 0.20 TiO, 0.26 Fe₂O₃, 0.56 CaO, 0.30 MgO, and 4.90 calcination losses [16]. Mixed-layered minerals and impurities are present in the porcelain stone PS in addition to the main minerals, quartz and kaolinite.

The inoculum and a modified Ashby's nutrient medium with the following composition (g/liter) were introduced into the PS suspension: saccharose — 52; (NH₄)₂SO₄ — 0.2; K₂HPO₄ — 1; Mg(SO₄) — 0.2. The suspension was kept for 30 days at temperature 23 – 25°C (aging process).

A stable cenosis of aerobic and anaerobic microorganisms taken from Prosyanskoe kaolin was used as the inoculum. Cultures forming a microbe community with pre-determined dominant forms served as the inoculating material. The community was maintained by re-inoculating on a sterile suspension of kaolin with added nutrient medium.

After the suspension of PS was allowed to age (stagnant water regime) several steps of enrichment of the suspension were conducted: magnetic separation and washing with water and an ammonium oxalate solution (washing regime).

The technological scheme for enriching PS consisted of several steps. Before aging the PS was comminuted in a jaw crusher to particle size about 3 mm and then subjected to wet grinding with moisture content 60% in a ball mill (sample 1). The kaolin suspension was processed in an SM 14 magnetic separator at different steps of enrichment with the magnetic and nonmagnetic fractions separated: after grinding — the nonmagnetic fraction (sample 2); after aging and washing with water (sample 3) — nonmagnetic fraction (sample 4); after washing with a solution of ammonium oxalate (sample 5) — nonmagnetic fraction (sample 6).

The chemical composition of the PS, including total iron oxides Fe₂O₃, was determined in a CMP-25 multichannel x-ray spectrometer (Table 1).

The EPR spectra of the PS samples were recorded with an RE-1306 radio spectrometer at frequency 9370 MHz at room temperature. The intensity of the wide signal in the region $g \sim 2.0 - 3.0$ associated with iron (hydr)oxide is determined in arbitrary units (see Table 1).

The reflection spectra of the samples were measured with a Pul'sar spectrophotometer with $d/8$ geometry neglecting the specular component (light source C, ICO 1931 observer). The color coordinates are represented in the ICO system

$$L^*a^*b^* 1976,$$

where L^* is the brightness and a^* , b^* are the chromaticity coordinates, where a^* , b^* denote the values of the saturation C_{ab}^* and hue h_{ab} , respectively. The hue h_{ab} equals 0 and 360 for red color and 90, 180 and 270 for yellow, green or blue. The saturation C_{ab}^* makes it possible to judge the amount of pure achromatic color.

The reducing capacity RC of iron oxides reflects the amount and composition of Fe(III) oxides (see Table 1). The magnetic susceptibility was measured with a KLY-2 Kappa-bridge system. Heating in the muffle furnace in a reducing medium was conducted to 550°C. The reducing capacity RC can be calculated from the following relation [16]:

$$RC = \chi_{\max} - \chi_0,$$

where χ_0 and χ_{\max} are the specific magnetic susceptibility before and after heat-treatment, respectively.

RESULTS AND DISCUSSION

Iron removal at different steps of enrichment. The first enrichment step is magnetic separation of the PS suspension (sample 1) and gives a nonmagnetic fraction (sample 2). This step makes the largest contribution to a reduction of RC

from 44×10^{-6} to 23×10^{-6} cm³/g (47.4%³) with a very small reduction of the Fe₂O₃ content from 0.27 to 0.26% (3.7%³) and yellowness Δb^* (0.29), which is due to the removal of large (hydr)oxide particles possessing comparatively large RC but having little effect on the coloristic characteristics. After calcination such particles, as a rule, do not dissolve completely in the amorphous phase and create defects in form of dark spots.

At the second enrichment step the PS suspension is allowed to age, which is followed by decantation of the dispersion medium and washing with water (sample 3). This step makes an average contribution to Fe₂O₃ (11.1%) and RC (25.0%) reduction.

The aging period of the PS suspension can be conventionally divided into two steps:

- the first step of the aging process (1 – 14 days) for the PS suspension is accompanied by lactic-acid fermentation, white foam is first to appear on the surface of the suspension and is followed by a ginger colored film which subsequently vanishes; at the first step the state of the PS, according to the values of the redox potential rH [1, 10], changes from moderately reducing rH = 23 to reducing rH = 12, favorable for the development of strictly anaerobic bacteria [2, 12];

- during the second step the reduced state is maintained to the end of the aging period and the color of the solid phase of the suspension changes from light-yellow to dark-gray.

Therefore, during the aging period of the PS suspension the values of two criteria change [1, 10]: the redox potential of the medium and the color of the solid phase, which attests to the occurrence of biochemical processes similar to gleification.

After the aging, washing with water and drying the color coordinates a^* and b^* of the PS (sample 3) changed very little (Fig. 1). It can be supposed that the water soluble iron compounds newly formed during gleification and removed during washing of the PS comprise only a small fraction.

After washing with water the PS suspension was separated into two parts: one part went through the magnetic separation step — step 3A — with separation into two fractions: magnetic and nonmagnetic (sample 4); the other part — state 3B — consisted of washing with a solution of ammonium oxalate (sample 5) followed by magnetic separation (sample 6).

Magnetic separation of the PS suspension after aging and washing with water — step 3A — makes a small contribution to the reduction in the Fe₂O₃ content (3.7%) and change in yellowness ($\Delta b^* = 0.2$) of the nonmagnetic fraction (sample 4).

There are differences between the magnetic properties of the nonmagnetic and magnetic fractions of PS before and after aging:

- first, after aging the values of the magnetic susceptibility χ and the reducing capacity RC of the magnetic frac-

tion are greater than the corresponding values of the magnetic fraction before aging ($\chi = 2 \times 10^{-6}$ cm³/g versus $\chi < 0$ and RC = 36×10^{-6} cm³/g versus RC = 8×10^{-6} cm³/g, respectively); positive values of χ of the magnetic fraction after the PS has aged could attest to an improvement of the magnetic separation as well as the synthesis of new materials, probably, magnetite, which promotes magnetic flocculation;

- second, the reducing capacity RC of the nonmagnetic fraction after aging (sample 3) is less than the corresponding values of the nonmagnetic fraction before aging (sample 2) and after magnetic separation (sample 4) (RC = 13×10^{-6} cm³/g versus RC — 16×10^{-6} cm³/g, respectively);

- third, an increase in the intensity of the wide signal $g \sim 2.0 - 3.0$ in the EPR spectrum of the post-aging PS samples from 0.95 (sample 2) to 1.70 arb. units (sample 3) indirectly attests to the separation of iron (hydr)oxides from the volume of mineral aggregates during disaggregation.

It is entirely likely the biogenic magnetite is formed by Lovely's scheme owing to the solid-phase transformation of sorbed Fe(II) on the surface of the hydroxides [8]:



The formation of magnetite as a product of biogenic reduction of iron hydroxide is confirmed by thermodynamic calculations [17] and agrees with experimental data.

A characteristic feature of the initial PS (sample 1) is weak separability of iron minerals. For this reason the magnetic fraction is strongly contaminated by diamagnetic minerals and, correspondingly, $\chi < 0$. The increase of the magnetic susceptibility of the magnetic fraction separated after aging of PS as compared with the magnetic fraction separated from the initial PS sample is possible owing to the destruction of contacts between particles of the diamagnetic minerals of PS and the iron minerals under the action of microorganisms and their metabolites as well as owing to the flocculation of iron minerals. As a result, the fraction of iron minerals which are no longer bound with diamagnetic minerals increases. In addition to this effect, the presence of a small magnetite fraction in the magnetic fraction of PS, in general, increases the magnetic susceptibility to $\chi > 0$ very little. According to the high values of the RC, aside from magnetite iron (hydr)oxides are also found in the magnetic fraction after aging. Intense magnetic flocculation occurs in a magnetic field during separation; the mechanism of this process is presented in [18]. The newly formed Fe(II) compounds are very sensitive to an increase of the redox potential of the medium. During magnetic separation the PS suspension comes into contact with air and the reducing capacity of the PS of the nonmagnetic fraction (sample 4) increases somewhat.

Biological processes have their own particularities, owing to which the conditions of dissolution of (hydr)oxides during gleification differ from the chemogenic conditions [8]. The main factor in the rate of bacterial reduction of iron

³ The reduction, %, in the values of RC and Fe₂O₃ relative to the values of the preceding samples are presented here and below.

hydr(oxides) is the specific surface area of the particles [15, 19]. For this reason, during biological reduction, first the fine weakly crystallized particles are subjected to dissolution and the large crystalline (hydr)oxides are preserved. When the contacts between the iron minerals and the diamagnetic minerals of the PS break down the iron (hydr)oxides are easily removed during magnetic separation with cooperation between the microorganisms. But, since the magnetic separation after biotreatment of the PS has only a very small effect, it can be assumed that after the PS has aged the crystallized particles of iron minerals comprise only a small fraction.

The oxidation and hydrolysis of Fe(II) are accompanied during washing with water by synthesis of newly formed, weakly ordered Fe(II) iron minerals, which, on the one hand, are separated less effectively during magnetic separation and, on the other hand, increase the fraction of oxalate dissolvable iron minerals [1].

Washing of the PS suspension (sample 3) with an ammonium oxalate solution — step 3B — decreases the Fe_2O_3 content significantly (18.5%) and the RC very little (9.1%) with a large reduction of yellowness ($\Delta b^* = 3.3$) (sample 5) after drying.

It was shown in the course of the experiments on gleification of PS that on the one hand gleification leads to a reduction of the magnetic susceptibility of iron compounds in PS, while on the other hand the solubility of iron (hydr)oxides in ammonium oxalate increases. According to [20] the presence of oxalate during the washing regime accelerates the reduction and dissolution of (hydr)oxides in the CM.

After magnetic separation of the PS suspension (sample 5) — step 4, the Fe_2O_3 content decreases by 7.4% and the values of RC of the nonmagnetic fraction decrease to the minimum value $2 \times 10^{-6} \text{ cm}^3/\text{g}$ (sample 6) as compared with the values for the initial samples (sample 1). The values of the yellowness b^* of this sample likewise decrease to the minimum 3.7 versus the values for the initial sample 8.8.

In summary, complex processing of PS reduces the total Fe_2O_3 by 40.7% compared with the initial value with different steps of the enrichment process making different contributions: magnetic separation 3.7%, after aging 3.7% and ultimately 7.4%; washing with water 11.1%; washing with a solution of ammonium oxalate 18.5% and subsequent magnetic separation 7.4%. Therefore, the following operations make the main contribution to the removal of iron after biotreatment of PS: washing with an ammonium oxalate solution > washing with water > magnetic separation.

Transformation of iron minerals during the treatment process and their effect on the color of porcelain stone. The values of the ICO color coordinates $L^*a^*b^*$ of the PS samples calcined in air at temperature 1300°C in an electric furnace and in a chamber furnace with a reducing gas medium. The whiteness W_g (GOST 24768) of the calcined samples of PS after removal of the iron increases from 6.5 to 19.0%, respectively.

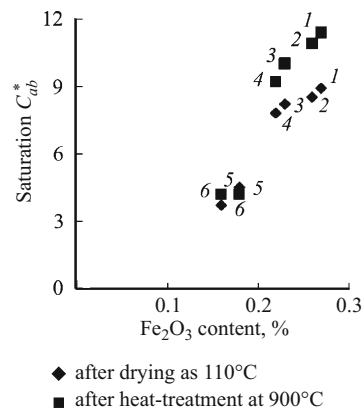


Fig. 1. Variation of the color saturation C_{ab}^* and the Fe_2O_3 content (wt.%) in PS samples versus the conditions of their enrichment and heat-treatment: 1 – 6) sample number.

Comparing the values of the color saturation C_{ab}^* (ICO $L^*a^*b^*$) of PS samples processed at all steps of enrichment and heat-treated at different temperatures and under different conditions of the gas medium shows the following:

- the color saturation of the PS samples decreases successively from the initial sample 1 to the sample 6; this is associated with a reduction of the Fe_2O_3 content (from 0.27 to 0.16%) and of the reducing capacity RC of iron (hydr)oxides (see Table 1), irrespective of the heat-treatment conditions (Fig. 1);

- the color saturation C_{ab}^* of the samples 1 – 4 depends on the conditions of biological and chemical treatment of the PS; this is associated with the content of Fe minerals and the change in the structural-chemical state of the iron impurities; after the PS ages and is washed with water the water-soluble Fe compounds are removed (sample 3), and after magnetic separation the particles of iron (hydr)oxides suspended in the dispersion medium are removed (sample 4); the main fraction of the iron is in the form of particles in the amorphous and weakly crystallized state Fe_{ox} , which possess a large specific surface area, dissolve more easily in the melt during calcination, and after calcination transform from super- and paramagnetic into a magnetically dilute state; the coloring power of iron in the magnetically dilute state of the compounds is low and, correspondingly, the color saturation C_{ab}^* of the PS samples decreases;

- the maximum difference in the saturation ΔC_{ab}^* between the PS samples depends on the composition of the gas medium used for heat-treatment (Fig. 2);

- the difference of the saturation ΔC_{ab}^* between the samples 3 and 5 is maximum after heat-treatment at 110, 900°C and calcination at 1300°C in air (3.3, 5.09 and 1.0, respectively), which is completely explainable (see Figs. 1 and 2); after PS ages and is washed with water (sample 3) and subjected to magnetic separation (sample 4) a very small fraction of Fe_b is removed, and after the PS is washed (sample 3)

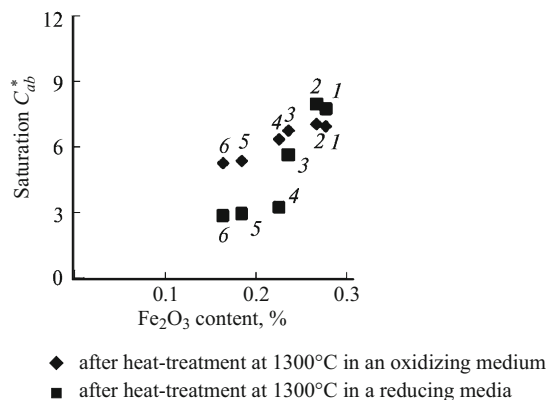


Fig. 2. Variation of the color saturation C_{ab}^* and the Fe_2O_3 content (wt.%) in PS samples versus the conditions of their enrichment and heat-treatment at 1300°C in oxidizing and reducing media: 1 – 6) sample number.

with a solution of ammonium oxalate (sample 5) the Fe_2O_3 content decreases significantly, so that the difference between the third and fifth samples reaches the maximum value;

– in the case of calcination at 1300°C in a reducing gas medium the maximum difference in terms of the saturation occurs between the samples 2 and 3 as well as between the samples 3 and 4 (2.4 and 2.3, respectively) (Fig. 2); for calcination in a reducing gas medium the reduction of the saturation ΔC_{ab}^* is due to the reduction $Fe(III) \rightarrow Fe(II)$ and, correspondingly, a reduction of the yellowness Δb^* ; it is entirely likely that after aging the structural-chemical organization of the main fraction of the iron compounds changes: the sizes of the newly formed iron $Fe(III)$ particles decrease and as a result the surface area increases, and such particles are more easily reduced in a reducing gas medium.

The color of the PS samples after heat-treatment at 900°C depends on the enrichment step relative to the color of these samples after drying (see Table 2). The brightness increases in all samples (ΔL^* from 2.2 to 5.1) and the color hue h_{ab} of the samples 1 – 4, right up to washing with ammonium oxalate, changes as follows: before heat-treatment — greenish-yellow (h_{ab} from 90 to 93), and after heat-treatment — reddish-yellow (h_{ab} from 75 to 80); the hue h_{ab} of the samples 5 and 6 remains practically unchanged — greenish-yellow (h_{ab} from 91 to 94).

Therefore, right up to washing with ammonium oxalate the PS contains predominately iron minerals, whose color is yellow, changing to reddish-yellow after heat-treatment. The iron minerals giving to the materials a yellow color include iron hydroxides: goethite, ferrihydrite, ferroxigite, and others, while the reddish-yellow color is due to hematite. The color hue of the hematite depends strongly on the particle size: from red for well-crystallized particles to yellow-red for amorphous and poorly crystallized particles. After washing with ammonium oxalate (samples 5 and 6) most of the iron

TABLE 2. Change in the Color Characteristics of PS versus the Conditions of Biochemical and Thermal Treatment

Sample	Color coordinates, ICO 1976				
	L^*	a^*	b^*	C_{ab}^*	h_{ab}
After drying at 110°C					
1	86.15	−0.77	8.83	8.86	90.03
2	87.33	−0.19	8.54	8.55	91.36
3	89.95	−0.41	8.00	8.20	92.93
4	89.99	−0.10	7.80	7.78	93.00
5	90.20	−0.10	4.50	4.50	91.39
6	90.38	−0.16	3.70	3.72	93.58
After heat treatment at 900°C					
1	90.97	2.93	10.97	11.35	74.99
2	91.25	3.04	10.40	10.85	76.50
3	92.16	1.75	9.90	10.00	79.97
4	93.27	1.98	9.20	9.22	77.86
5	94.14	−0.31	4.15	4.16	94.34
6	95.47	−0.12	4.20	4.21	91.67
After calcination at 1300°C in air					
1	93.05	−0.10	7.04	7.04	90.90
2	92.65	0.11	7.12	7.12	89.02
3	92.88	0.15	6.80	6.80	88.66
4	93.73	0.01	6.40	6.40	89.93
5	94.66	0.41	5.35	5.38	90.55
6	94.77	−0.15	5.30	5.31	91.66
After calcination at 1300°C in a reducing medium					
1	90.95	−0.11	7.77	7.77	90.88
2	91.54	−0.42	8.04	8.06	93.08
3	90.65	−0.36	5.64	5.66	93.74
4	92.20	−0.74	3.26	3.34	102.90
5	90.50	−0.70	3.01	3.02	103.60
6	89.33	−0.73	2.82	2.90	104.50

in PS is in a magnetically dilute state and its color remains unchanged after heat-treatment at 900 and 1300°C in a neutral gas medium.

CONCLUSIONS

A technological scheme of a two-step method of removing iron from clayey material, including porcelain stone, was proposed on the basis of studies.

The whiteness of PS after iron removal increases depending on the heat-treatment regime. The color saturation C_{ab}^* (ICO $L^*a^*b^*$ 1976) of PS decreases after aging and bio-reduction of $Fe(III)$ with the subsequent iron-removal operations making differing contributions: washing with ammonium oxalate > magnetic separation > washing with water. The reduction of the color saturation C_{ab}^* is associated with a reduction of the iron content in the porcelain stone.

When PS is calcined at 1300°C in a reducing gas medium the saturation difference ΔC_{ab}^* reaches a maximum between samples before and after aging, while for a neutral gas medium the maximum is reached after aging followed by washing with ammonium oxalate. After aging the main fraction of iron compounds shows changes in structure-chemical organization, and probably the newly formed particles, which undergo reduction more easily in a reducing gas medium used for calcination, become smaller. After washing with ammonium oxalate most of the 'nonsilicate' iron is removed from the PS composition, and the remaining iron fraction — the magnetically dilute fraction — possesses a low coloring capacity and has practically no effect on the color characteristics.

Processes, similar to soil gleification and accompanied by the formation of anaerobic conditions of the medium with bioreduction of iron and synthesis of new materials, occur as the PS suspension ages under certain conditions.

After aging and magnetic separation of the PS the increase in the specific magnetic susceptibility of the magnetic fraction versus the corresponding values of this fraction before aging is related with the action of two factors: 1) destruction of the contacts between the Fe minerals and the particles of diamagnetic minerals, which is accompanied by an increase in the fraction of iron minerals in the magnetic fraction, and 2) magnetic flocculation of iron minerals under the action of the magnetic field and higher magnetic susceptibility of the aggregates of iron minerals.

The high solubility of the particles of iron minerals after gleification of the PS by ammonium oxalate is due to their weak ordering and high dispersity (high specific surface) as well as the redox potential of the dispersion medium and the Fe(II) content.

REFERENCES

1. R. A. Platova, G. N. Maslennikova, and Yu. T. Platov, "Biochemical method of removing iron from Zhuravliniy Log kaolin," *Steklo Keram.*, No. 2, 15–22 (2013); R. A. Platova, G. N. Maslennikova, and Yu. T. Platov, "Biochemical method of removing iron from Zhuravliniy Log kaolin," *Glass Ceram.*, **70**(1–2), 51–56 (2013).
2. T. C. Eisele and K. L. Gabby, "Review of Reductive Leaching of iron by Anaerobic Bacteria," *Mineral Proc. Extractive Metall. Review: Int. J.*, **35**(2), 75–105 (2014); Placed on site June 11, 2012, published on site July 22, 2013.
3. J. A. Gonzalez and M. del C. Ruiz, "Bleaching of kaolins and clays by chlorination of iron and titanium," *Applied Clay Sci.*, **33**(3–4), 219–229 (2006).
4. F. Veglio, "Factorial experiments in the development of a kaolin bleaching process using thiourea in sulphuric acid solutions," *Hydrometallurgy*, **45**(1–2), 181–197 (1997).
5. V. R. Ambikadevi and M. Lalithambika, "Effect of organic acid on ferric iron removal from iron-stained kaolinite," *Applied Clay Sci.*, **16**(3–4), 133–145 (2000).
6. A. Tuncuk, S. Ciftlik, and A. Akcil, "Factorial experiments for iron removal from kaolin by using single and two-step leaching with sulfuric acid," *Hydrometallurgy*, **134–135**, 80–86 (2013).
7. S. Oh Lee, T. Tran, B. Hi Juhg, et al., "Dissolution of iron oxide using oxalic acid," *Hydrometallurgy*, **87**(3–4), 91–99 (2007).
8. U. Schwertmann, "Solubility and dissolution of iron oxides," *Plant and Soil*, **130**(1–2), 1–25 (1991).
9. Yu. N. Vodyanitskii, *Chemistry, Mineralogy and Color of Gleified Soils* [in Russian], GNU Pochvennyi Institut im. V. V. Dokuchaeva, Russian Academy of Agricultural Sciences, Moscow (2006).
10. R. A. Platova and G. N. Maslennikova, "Biochemical nature of gleification during aging of clayey materials (review)," *Steklo Keram.*, No. 9, 14–20 (2009); R. A. Platova and G. N. Maslennikova, "Biochemical nature of gley formation during aging of clayey materials (review)," *Glass Ceram.*, **66**(9–10), 318–323 (2009).
11. R. A. Platova, A. N. Chernyshov, and G. N. Maslennikova, "Biotreatment of clayey materials and ceramic pastes: directions, methods and experience (review)," *Steklo Keram.*, No. 7, 15–22 (2012); R. A. Platova, A. N. Chernyshov, and G. N. Maslennikova, "Biotreatment of clayey materials and ceramic pastes: directions, methods and experience (review)," *Glass Ceram.*, **69**(7–8), 229–235 (2009).
12. Y-Su Luu and J. A. Ramsay, "Review: microbial mechanisms of accessing insoluble Fe(III) as an energy source," *World Journal of Microbiology and Biotechnology*, **19**(2), 215–225 (2003).
13. D. R. Lovley, "Dissimilatory Fe(III) and Mn(IV) reduction," *Microbiological Rev.*, **55**(2), 259–287 (1991).
14. D. R. Lovley, "Extracellular electron transfer: wires, capacitors, iron lungs, and more," *Geobiology*, No. 6, 225–231 (2008).
15. E. E. Roden and M. M. Urrutia, "Influence of biogenic Fe(II) on bacterial crystalline Fe(III) oxide reduction," *Geomicrobiol. J.*, **19**(2), 209–251 (2002).
16. G. N. Maslennikova, R. A. Khalilullova, and Yu. T. Platov, "Identification of iron compounds in clay-containing materials," *Steklo Keram.*, No. 2, 12–15 (1999); G. N. Maslennikova, R. A. Khalilullova, and Yu. T. Platov, "Identification of iron compounds in clay-containing materials," *Glass Ceram.*, **56**(1–2), 48–51 (1999).
17. J. K. Fredrickson, J. M. Zachara, D. W. Kennedy, et al., "Biogenic iron mineralization accompanying the dissimilatory reduction of hydrous ferric oxide by a groundwater bacterium," *Geochim. Cosmochim. Acta*, **62**(19–20), 3239–3257 (1998).
18. M. A. Nakhamkin and G. I. Zhuravlev, "On ferromagnetic filtration of ceramic suspensions," *Steklo Keram.*, No. 7, 25–27 (1977); M. A. Nakhamkin and G. I. Zhuravlev, "Ferromagnetic filtration of ceramic suspensions," *Glass Ceram.*, **34**(8), 508–511 (1977).
19. C. Liu, S. Kota, J. M. Zachara, et al., "Kinetic analysis of the bacterial reduction of goethite," *Environ. Sci. Technol.*, **35**, 2482–2490 (2001).
20. Q.-X. He, X.-Ch. Huang and Z.-L. Chen, "Influence of organic acids, complexing agents and heavy metals on the bioleaching of iron from kaolin using Fe(III)-reducing bacteria," *Applied Clay Sci.*, **51**(4), 478–483 (2011).